Abstract No: 2025_436

Sustainable Optimization of Modifier-Free Graphite Furnace Atomic Absorption Spectrophotometric Method for Trace Cadmium Determination in Seawater

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The determination of trace cadmium (Cd) in seawater is analytically challenging due to the high salinity of marine matrices, which induces significant non-specific absorption and spectral interferences in Graphite Furnace Atomic Absorption Spectrometry (GFAAS). Conventional methods rely on chemical modifiers to stabilize the analyte and suppress matrix effects; however, these additives increase analytical cost, introduce contamination risks, and conflict with the principles of Green Analytical Chemistry. This study presents the development of a sustainable, modifier-free GFAAS method for cadmium determination in seawater, coupled with a rigorous evaluation of measurement uncertainty to ensure metrological reliability. Cadmium analysis was performed using Zeeman-effect corrected GFAAS. Artificial seawater was prepared according to ASTM D1141-98 to simulate a marine matrix, and graphite furnace parameters were systematically optimized using a one-variable-at-a-time approach to reduce matrix interferences. The optimized temperature program (drying/pyrolysis/atomization: 150/800/1400 °C) substantially improved analytical performance. In comparison with the manufacturer's default program, the cadmium recovery increased markedly from 4.7% to 85.1% without the use of chemical modifiers. A further 2-fold dilution of the sample enhanced recovery to 103.7%, indicating effective mitigation of matrix effects. External calibration, matrix-matched calibration, and standard addition methods were assessed for quantification. External calibration under optimized conditions provided reliable results, while matrix-matched calibration showed signal enhancement effects. A comprehensive measurement uncertainty assessment was conducted in accordance with Eurachem/CITAC guidelines. The method demonstrated satisfactory analytical performance, with repeatability identified as the dominant contributor to the overall uncertainty budget yielding an expanded uncertainty of ±0.63 µg/L, equivalent to a relative uncertainty of 6.3%. The method achieved a limit of detection of 0.76 µg/L and is therefore suitable for routine monitoring of cadmium in seawater. The developed modifier-free GFAAS method provides a sustainable, cost-effective, and reliable approach for trace cadmium determination in seawater. By eliminating chemical modifiers while maintaining satisfactory analytical performance, the method supports Green Analytical Chemistry principles and offers a practical tool for routine environmental monitoring and desalination-related applications.

Keywords:

Cadmium, Seawater, GFAAS, Measurement uncertainty, Optimized Temperature Program

Acknowledgment:

The authors gratefully acknowledge the National Water Supply and Drainage Board, Jaffna for providing the facilities and support to conduct this research.